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Tetrazolo[1,5-a]pyridines and Furazano[4,5-b]pyridine-1-oxides as Energetic Materials

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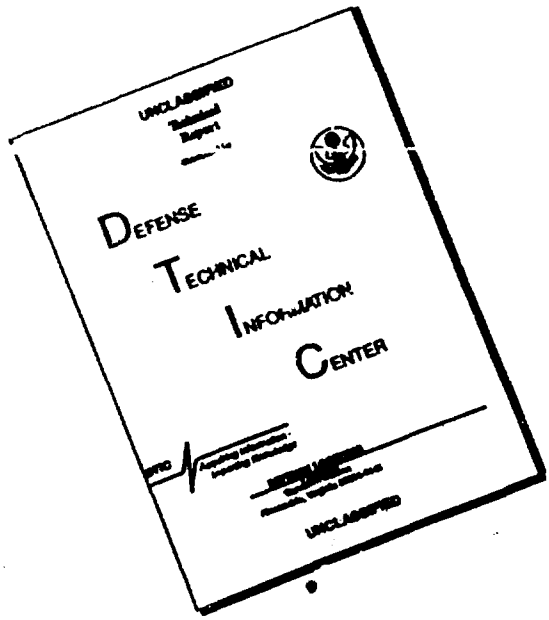

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FOREWORD

There is a continuing need for new energetic materials with improved performance and/or enhanced stability and sensitivity. A class of compounds which has been little investigated is comprised of polynitroheterocycles. This report examines tetrazolo-[1,5-a]pyridines and furazano[4,5-b]pyridine-1-oxides, with particular reference to their synthesis, structure, stability, and sensitivity.

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This report has been reviewed for technical accuracy by Richard A. Hollins.

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19. ABSTRACT (*Continue on reverse if necessary and identify by block number*)

The synthesis of a series of tetrazolo[1,5-a]pyridines by nucleophilic azide attack on 2-chloropyridines is described. The chemistry of these compounds is also discussed, with particular reference to their thermal stability and their equilibria with the corresponding 2-azidopyridines. The explosive properties of 4,6-dinitrotetrazolo[1,5-a]pyridine are presented. This material shows moderate explosive properties, but is thermally unstable. The synthesis of furazano[4,5-b]pyridine-1-oxides by thermolysis of 4-nitrotetrazolo[1,5-a]pyridines is described, as are their structures and chemical properties. The explosive properties of 6-nitrofurazano[4,5-b]pyridine-1-oxide are also discussed. This material shows explosive and thermal properties comparable with those of trinitrotoluene. The synthesis of tetrazolo[1,5-f]-furazano[4,5-b]pyridine-1-oxide by nucleophilic azide attack on 3-nitro-2,6-dichloropyridine is also described. The structure of this compound has been elucidated, and its explosive properties are described. It exhibits properties typical of a primary explosive, while being thermally stable to about 135°C. This compound provides a potential route to further nitrogen substitution of the pyridine ring, possibly opening up a new class of energetic materials.

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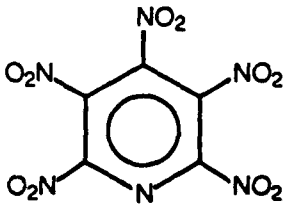
INTRODUCTION

Over a period of several years, highly substituted polynitroaromatics have been investigated as a source of new dense and energetic explosives. These investigations have been moderately successful, producing such materials as hexanitrobenzene (Reference 1), pentanitrotoluene (Reference 2), and decanitrobiphenyl (Reference 3). However, while these compounds have realized the predicted high densities and explosive energies, they have also tended to be thermally unstable and somewhat sensitive.

A related class of compounds, which has not been extensively investigated, is comprised of the polynitroheterocycles. For example, pentanitropyridine (**1**) and pentanitropyridine-N-oxide (**2**) are predicted to have densities (Reference 4) of 1.95 and 2.01, detonation velocities (Reference 5) of 9290 and 9050 m/s, and detonation pressures (Reference 5) of 411 and 388 kbar, respectively, while 3,5-diamino-2,4,6-trinitropyridine (**3**), with a density of 1.81, a detonation velocity of 8470 m/s, and a detonation pressure of 334 kbar, might be expected to have stability and sensitivity resembling 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) and 2,4-diamino-1,3,5-trinitrobenzene (DATB). Unfortunately, the methods utilized so successfully in the benzenoid series have failed when applied to heterocycles, and new strategies must therefore be developed.



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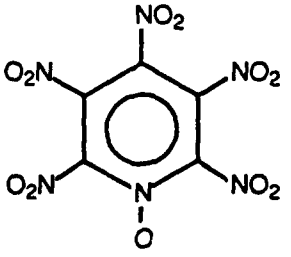

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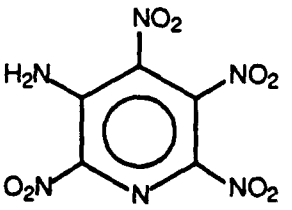

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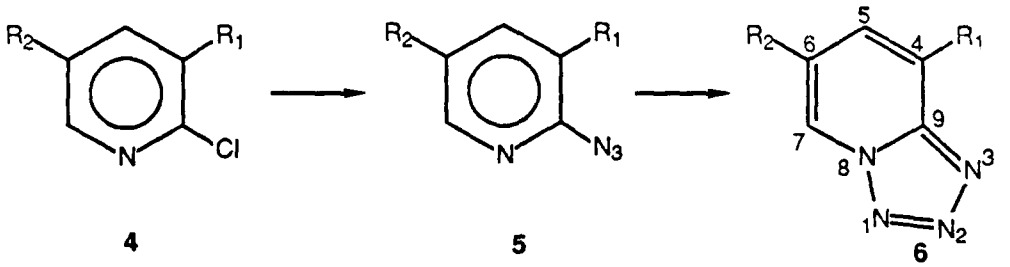
A related family of compounds, the study of which should give further insight into polynitroheterocyclic systems, is the tetrazolo[1,5-a]pyridines. These materials should exhibit useful explosive properties, without however matching those predicted for the polynitropyridines. In addition they should provide access to the pyridofuroxans (more properly furazano[4,5-b]pyridine-1-oxides), attractive by analogy with the useful and energetic benzofuroxans (References 6-9). Further, oxidation of the pyridofuroxans may open up a new route to the polynitropyridines.

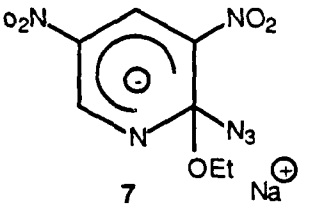
RESULTS AND DISCUSSION

2-Chloropyridines have been shown to react with sodium azide in the presence of hydrochloric acid to give the corresponding tetrazolo[1,5-a]pyridines (Reference 10). The reaction, of course, proceeds by initial nucleophilic displacement of chlorine by the azide ion, followed by an electrocyclic ring closure. Predictably, the presence of an electron-withdrawing nitro-group at the 3- or 5-position aids the initial azide displacement, and whereas the reaction of 2-chloropyridine (**4a**) itself must be carried out in dimethylformamide (DMF) under reflux, the corresponding reactions of 3-and 5-nitro-2-chloropyridines (**4b,c**) proceed smoothly and in high yield in refluxing ethanol. Indeed 2-chloro-3,5-dinitropyridine (**4d**) reacts with hydrazoic acid in ethanol at ambient temperature. (In the absence of acid, **4d** reacts with sodium azide in ethanol to form the Meisenheimer-type complex (**7**), which is converted to the desired product by treatment with hydrochloric acid in ethanol.)



4 **5** **6**

a $R_1 = R_2 = H$
b $R_1 = NO_2$; $R_2 = H$
c $R_1 = H$; $R_2 = NO_2$
d $R_1 = R_2 = NO_2$



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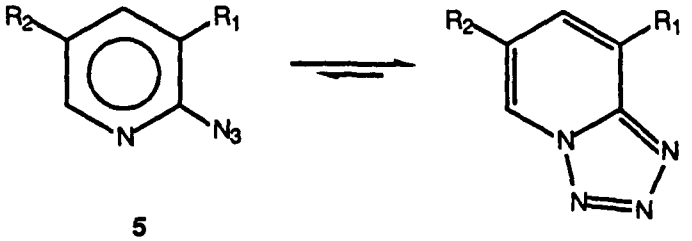
However, the presence of the nitro-groups also affects the cyclization to form the tetrazolopyridine. The azidopyridine and the tetrazolopyridine are in equilibrium. In the case of the unsubstituted compound, the equilibrium is far to the right. No trace of the azido-compound **5a** can be detected in the infrared (IR) or nuclear magnetic resonance (NMR) spectra, although the loss of 28 mass units provides the base peak of the mass spectrum and the generation of the pyridine-2-nitrene (**8**) has been cited in the pyrolysis of tetrazolopyridine (Reference 11). Similarly 4-nitrotetrazolo[1,5-a]-pyridine (**6b**) appears to be free of the azido-isomer (**5b**), with no trace of the latter being visible in the IR and NMR spectra. Once again, however, the mass spectrum of **6b** showed a prominent peak at 137, which was attributed to the loss of molecular nitrogen. On the other hand, the NMR spectrum of 6-nitrotetrazolo[1,5-a]pyridine (**6c**) in d_6-acetone showed the presence of the azido-compound (**5c**) at the level of 10%. Even more pronounced, the product from the reaction of hydrazoic acid with 2-chloro-3,5-dinitropyridine (**4d**), when dissolved in d_6-acetone, contains a mixture of two compounds identified as 4,6-dinitrotetrazolo[1,5-b]pyridine (**6d**) and the azido-isomer (**5d**) present to the extent of some 40%. These results are presented in Table 1, and have been conveniently explained in terms of the electron-withdrawing nitro-groups at

the 4- and 6-positions destabilizing the electronegative tetrazole ring in favor of the azido-group. The failure to detect any evidence for **5b** would appear to be anomalous.



5 **6**

a $R_1 = R_2 = H$
b $R_1 = NO_2$; $R_2 = H$
c $R_1 = H$; $R_2 = NO_2$
d $R_1 = R_2 = NO_2$

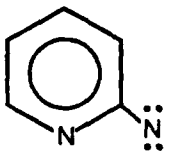


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TABLE 1. Equilibrium of Tetrazolo[1,5-a]pyridines with 2-Azidopyridines in d_6-Acetone Solution.

Tetrazolo[1,5-a]pyridine	2-Azidopyridine Present
6a	**5a**, 0 %
6b	**5b**, 0 %
6c	**5c**, 10 %
6d	**5d**, 40 %

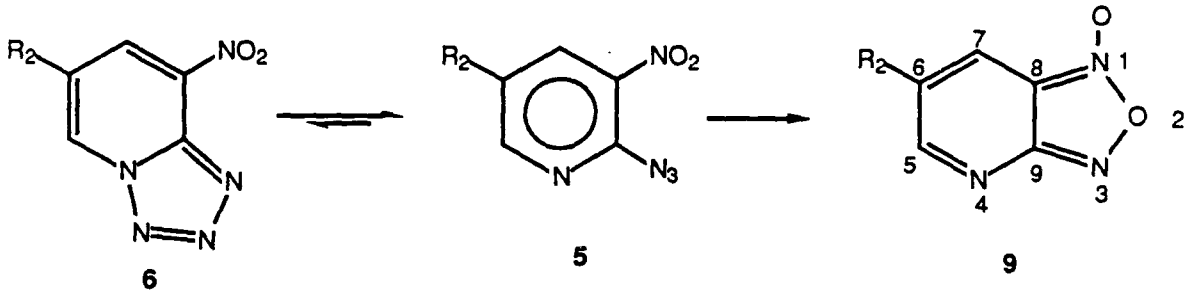
The presence of the azidopyridine (**5d**), in association with the tetrazolopyridine (**6d**), in acetone solution was confirmed by Fourier-transform infrared spectroscopy (FTIR) which showed an azido-absorption (doublet) at 2153 and 2143 cm^{-1} as well as three nitro-group bands at 1599, 1575, and 1553 cm^{-1}. The FTIR spectrum of a standard pressed KBr disc of the solid showed only two nitro-group bands, at 1575 and 1553 cm^{-1}, and no obvious azido band. However, diffuse reflectance FTIR spectroscopy, followed by careful re-examination of the standard spectrum, confirmed that the azido-isomer is indeed present in the solid state, at least in small quantities. In view of the simultaneous presence of the two forms in solution, and also to a lesser extent in the solid, it comes as no surprise that the material is extremely difficult to recrystallize. The best purification appears to be dissolution in aqueous ethanol, followed by evaporation of the ethanol at ambient temperature under high vacuum.

Equally predictably, the equilibrium between the two forms in solution is markedly affected by the solvent, as illustrated in Table 2. Thus, in deuterochloroform the azido-form (**5d**) is present at 100% to the exclusion of **6d**, while in d_6-DMSO **5d** is present to only 9%; the tetrazolopyridine is dominant at 91%.

TABLE 2. Equilibrium between 4,6-Dinitrotetrazolo-[1,5-a]pyridine and 2-Azido-3,5-dinitropyridine in Various Solvents.

Solvent	2-Azido-3,5-dinitropyridine, %
$CDCl_3$	100
C_6D_6	80
$(CD_3)_2CO$	40
CD_3CN	37.5
$(CD_3)_2SO_2$	9

This equilibrium is further complicated by the fact that 2-azido-3,5-dinitropyridine undergoes reaction in solution at ambient temperature. The nature of the reaction in d_6-acetone and -DMSO is still uncertain, but in deuterated chloroform, benzene, and acetonitrile, the azido-compound loses molecular nitrogen and recyclizes to form 6-nitrofurazano[4,5-b]pyridine-1-oxide (6-nitropyridofuroxan) (**9d**). The half-life for this reaction is about 3 days in chloroform or benzene and about 16 days in acetonitrile. The same conversion may be achieved by cautiously heating neat to 120°C, or more conveniently by heating in toluene under reflux until the gas evolution is completed. In a similar fashion the parent furazano[4,5-b]pyridine-1-oxide (pyridofuroxan) (**9b**) may be prepared by heating a toluene solution of **6b** under reflux, providing some evidence that the latter compound is also in equilibrium with the corresponding azido-isomer, at least at elevated temperatures.



b $R_2 = H$; d $R_2 = NO_2$

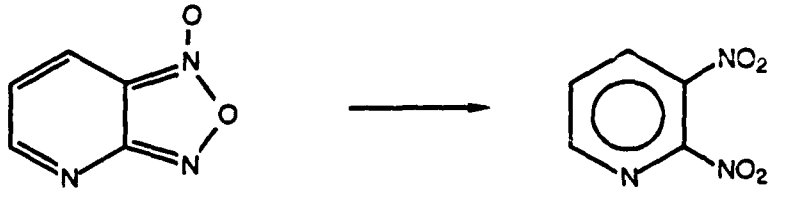
(The synthesis of benzofuroxans from o-chloronitrobenzenes--and of the pyridofuroxan (**9d**) from **4d**--in a one-pot phase-transfer reaction with sodium azide in dichloroethane has recently been described (Reference 12). Experiments in our own laboratories have indicated that in other solvent systems the phase-transfer catalyst may not be necessary (References 8 and 9). Carrying out the reaction under these conditions also precluded the isolation of the tetrazolopyridine (**6d**) intermediate in the formation of **9d**.)

Empirical calculations (References 4 and 5) suggest that 4,6-dinitrotetrazolo[1,5-a]pyridine (**6d**) should have a density of 1.79, and a detonation velocity and pressure of 8250 m/s and 314 kbar, respectively. However, it also appears to be rather sensitive to impact, being initiated quite easily in a simple hammer/anvil

screening test. This sensitivity to impact is possibly attributable to the presence of a small amount of the azido-isomer (**5d**) and may perhaps be reduced if a purification method can be devised to remove that material. Indeed "recrystallization" twice by dissolution in aqueous ethanol followed by stripping off the organic solvent under vacuum gave a material with a drop-weight impact sensitivity of 61.7 cm. However this material was a very fine, fluffy solid, and this low sensitivity may simply be due to the particle shale and size. In support of this proposal, a small sample of apparently more crystalline material had an impact sensitivity of 46.8 cm. On the other hand **6d** is also thermally unstable at about 122°C, and therefore is not of great utility as an explosive. The pyridofuroxan (**9d**) to which **6d** decomposes is predicted to have a density of 1.82, and a detonation velocity and pressure of 7300 m/s and 282 kbar, respectively. However, the density determined by gas pycnometry was only 1.74. It has a drop-weight impact sensitivity of 25.7 cm, and although it melts at 93°C it appears to be thermally stable to about 200°C.

Benzofuroxans (benzofurazan-1-oxides) (**10**) may be oxidized to substituted 1,2-dinitrobenzenes (**11**) by the action of 90% hydrogen peroxide in sulfuric or polyphosphoric acid, although the oxidation of benzodifuroxans is less successful (Reference 13). We hoped that application of a similar procedure might provide access to the 2,3-dinitropyridines. The pyridofuroxans proved to be more resistant to oxidation by reagents ranging in strength from chloroperbenzoic acid to peroxydisulfuric acid in 30% oleum. In no case could any sign of pyridine-N-oxide be detected, but the furoxan ring of **9b** was oxidized by peroxydisulfuric acid formed *in situ* from 90% hydrogen peroxide in 30% oleum, giving the previously unknown 2,3-dinitropyridine (**12**). However, 6-nitrofurazano[4,5-b]pyridine-1-oxide (**9d**) appears to be stable towards oxidation even under these conditions. This is a rather disappointing result, but the oxidation of **9d** will be investigated further.

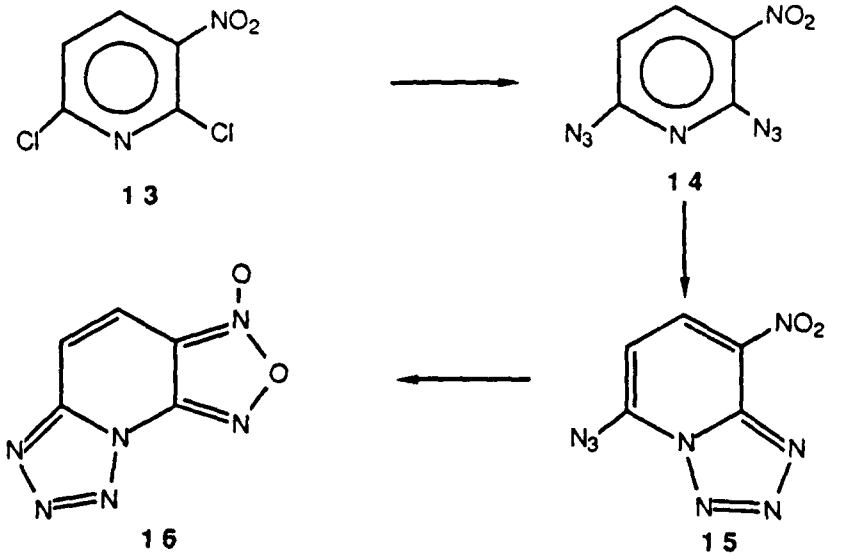
10 **11**



9b **12**

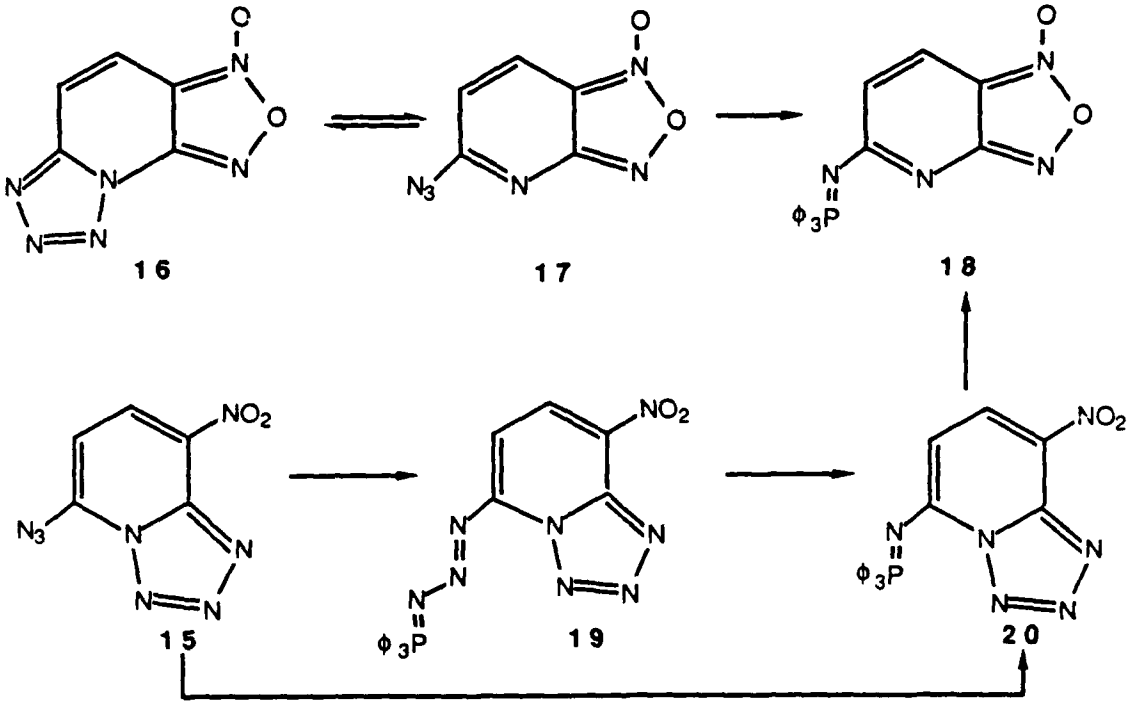
If the presence of nitro-groups at the 4- and 6-positions destabilizes the tetrazolo[1,5-a]pyridine ring system with respect to the 2-azidopyridine, it seemed reasonable that a furoxan ring fused at the 6- and 7-positions might stabilize it. Taking

advantage of the formation of both tetrazolo- and furazanopyridines described above, 3-nitro-2,6-dichloropyridine (**13**) was treated with sodium azide. In this case the best reaction medium seemed to be acetonitrile rather than acidic aqueous ethanol. If the reaction was carried out under reflux conditions, tetrazolo[1,5-f]furazano[4,5-b] pyridine-1-oxide (furoxanotetrazolopyridine) (**16**) was obtained directly. If the reaction was carried out at ambient temperature, an azido-tetrazolo[1,5-a]pyridine was isolated, contaminated with about 10% of **16**. The azido compound was characterized by IR and NMR spectroscopy, and the structure (**15**) (presumably being formed via the intermediate (**14**)) was proposed by analogy with previous results (Reference 11). Reaction of **13** with one equivalent of azide gave a 50:50 mixture of the azido compound (**15**) and the unreacted starting material, with no trace of a monochloro intermediate being detected. Clearly, the first azido group (or tetrazolo functionality) activates the remaining chloro group to more facile displacement. Thermolysis of **15** results in the formation of **16**, and this route probably affords the most efficient synthesis of this compound.



The structure (**15**) for the intermediate azidotetrazolo[1,5-a]pyridine was supported by analysis of the reaction with triphenylphosphine (Reference 14). The furoxanotetrazolopyridine (**16**) reacts with triphenylphosphine in ethanol under reflux to form the phosphinimine (**18**), perhaps through the intermediacy of the azidofuroxanopyridine (**17**). When **15** was treated with triphenylphosphine in ethanol at ambient temperature, conditions selected to avoid equilibrium with the diazido compound (**14**), an orange precipitate was produced. This material was identified as the Staudinger intermediate (**19**), which proved to be thermally unstable; the Staudinger intermediate (**19**) decomposed with the evolution of nitrogen when heated in ethanol under reflux to give the phosphinimine (**20**), a yellow solid. This material was also formed by the reaction of **15** with triphenylphosphine in benzene solution at ambient temperature. Heating **20**, or indeed **19**, in toluene under reflux afforded the phosphinimine **18**, thus, establishing the structure of **15**. Since **16** can form only one phosphinimine, and the same material may be derived from **15** using these mild conditions under which rearrangement is improbable, the position of the azido group must be

that shown in 15. However, it must be noted that the thermal instability and insolubility of **19** and **20** made purification of these compounds impossible, while their NMR and mass spectra are somewhat equivocal.

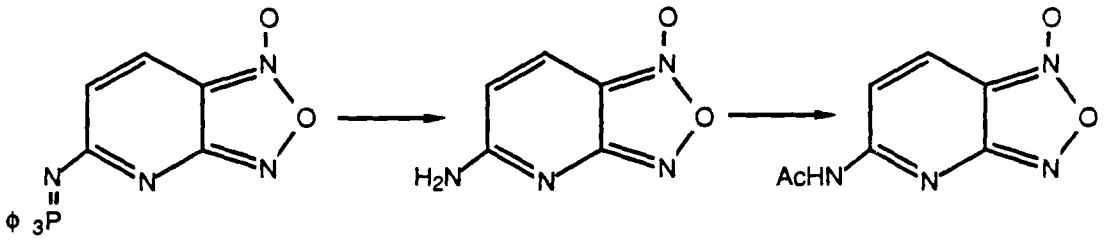


Tetrazolo[1,5-f]furazano[4,5-b]pyridine-1-oxide (**16**) is thermally stable below its melting point of 135°C but decomposes with a strong exotherm above that temperature. Empirical calculations predict a density of 1.82 and a detonation velocity of 7525 m/s. However, the density obtained by single crystal X-ray structure determination was only 1.72; clearly, these particular empirical calculations are inadequate for the pyridofuroxans. The crude hammer/anvil screening test indicated that **16** was also sensitive, and an impact sensitivity of 8.0 cm was obtained for this compound. This value is indeed typical of primary explosives and suggests the possibility of an equilibrium with the azidopyridofuroxan (**17**), although there is no evidence for its presence in the crystal structure of **16**. A re-examination of the NMR spectra of **16** confirmed such an equilibrium, at least in such solvents as acetonitrile, benzene, and chloroform. These results are summarized in Table 3.

TABLE 3. Equilibrium Between Tetrazolo[1,5-f]furazano-[4,5-b]pyridine-1-oxide (**16**) and Azidofuroxanopyridine (**17**) in Various Solvents.

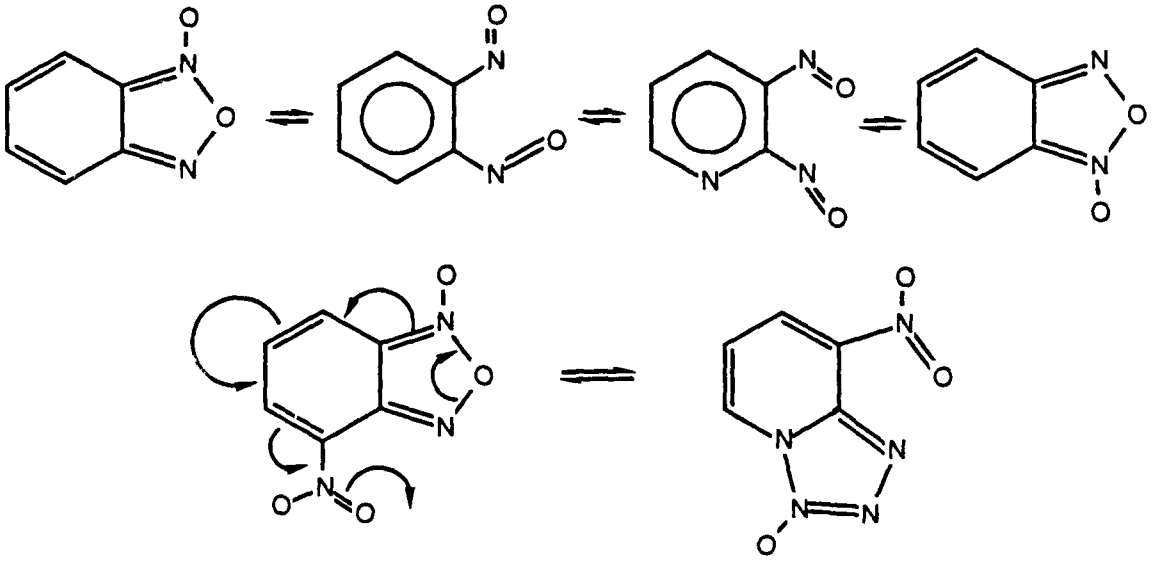
Solvent	Azidofuroxanopyridine, %
d_6-DMSO	0
d_6-Acetone	0
CD_3CN	6
C_6D_6	15
$CDCl_3$	39

Note that acid-catalyzed hydrolysis of the phosphinimine (**18**) yielded 5-aminofurazano[4,5-b]pyridine-1-oxide (**21**). This product was characterized as the acetyl derivative (**22**), and should provide access to further nitrogen-substituted pyridofuroxans. This possibility will be examined further in a subsequent publication.



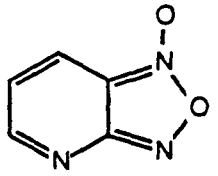
18 **21** **22**

Benzofuroxans exhibit a particularly rich and diverse chemistry, and notable within that chemistry is their propensity for tautomerism, with the exocyclic oxygen

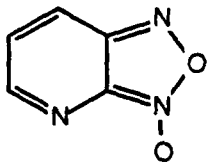


migrating between the 1- and 3-positions. Two different modes of rearrangement have been identified. In the first the furoxan ring undergoes electro-cyclic ring opening to an intermediate dinitrosobenzene, which rearranges before recyclizing in the opposite sense (Reference 15). The second mode of rearrangement is restricted to 4-nitro-benzofuroxans and occurs by a more extensive electrocyclic rearrangement involving both the furoxan ring and the nitro group (Reference 16). These reactions have manifested themselves both in dynamic equilibria between two positional isomers, and in the initial formation of kinetically favored isolable products and their subsequent rearrangement to thermodynamically favored isomers.

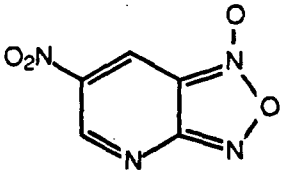
In the light of the rearrangements in the benzofuroxan series, the structure of the pyridofuroxans warrants further examination. These materials are obtained as pure single compounds, with no trace of the alternative isomer being detected in either the final product or the reaction mixture. Initially, the 1-oxide structures (**9b**, **9d**, **16**, **18**, **21**, and **22**) were assigned on the basis of the azido compounds from which they are ultimately derived. Intuitively, they would also appear to be the energetically more probable structures, but the alternative 3-oxide structures (**9b'**, **9d'**, **16'**, **18'**, **21'**, and **22'**) must be eliminated.



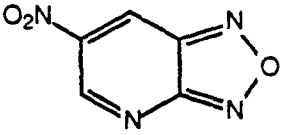
9b



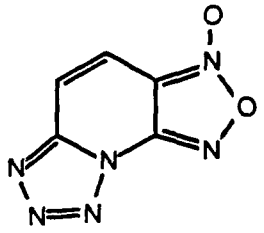
9b'



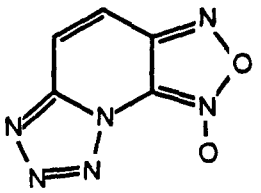
9d



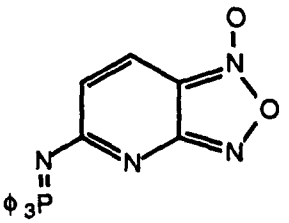
9d'



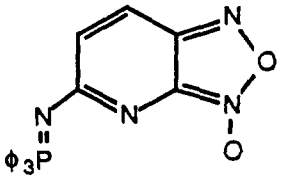
16



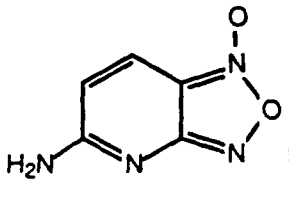
16'



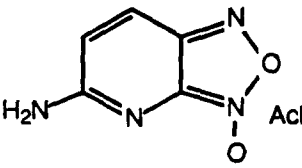
18



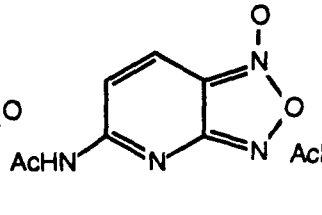
18'



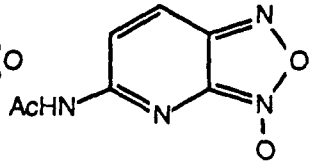
21



21'



22



22'

It is not readily apparent how to distinguish chemically between the 1-oxide and 3-oxide isomers. However, ^{13}C-NMR offers a possible solution to this problem. In a

^{13}C-NMR study involving a series of some 15 benzofuroxans, C_8 was found to have a chemical shift of 115 ±5, while C_9 had a chemical shift of 150 ±5 (Reference 17). Applying the same chemical shift increments to pyridine, the C_8 and C_9 chemical shifts of the furazano[4,5-b]pyridine-1-oxides should be about 110 and 170, while those for the 3-oxides should be about 144 and 136, respectively. In practice, for the group of 5 pyridofuroxans the mean chemical shifts were 109 and 159, respectively, strongly implicating the proposed 1-oxide structures. This conclusion was confirmed by single crystal X-ray structure determination on the tetrazolo[1,5-f]furazano[4,5-b]-pyridine-1-oxide (**16**). Unfortunately, suitable crystals of the other pyridofuroxans could not be prepared, but in **16** the exocyclic oxygen is clearly located on N_1. (This structure is illustrated in Figure 1, in which the atoms are labelled according to crystallographic convention rather than to International Union of Pure and Applied Chemistry (IUPAC) rules. Thus, N_1 becomes N(2). This numbering system is used throughout the following discussion of the single crystal X-ray structure results.)

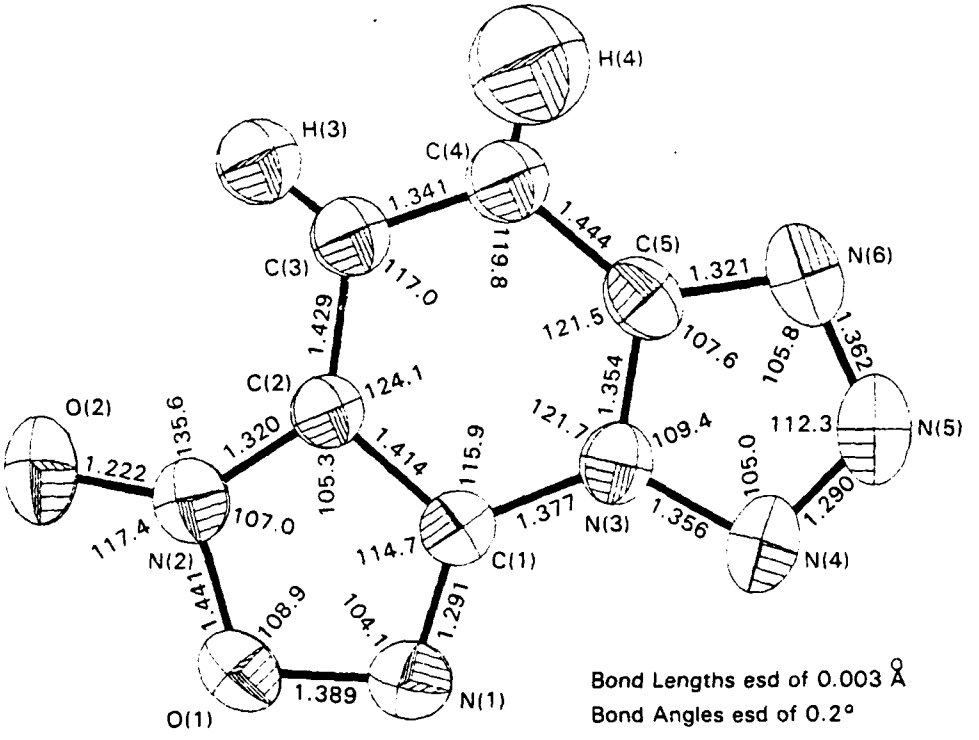
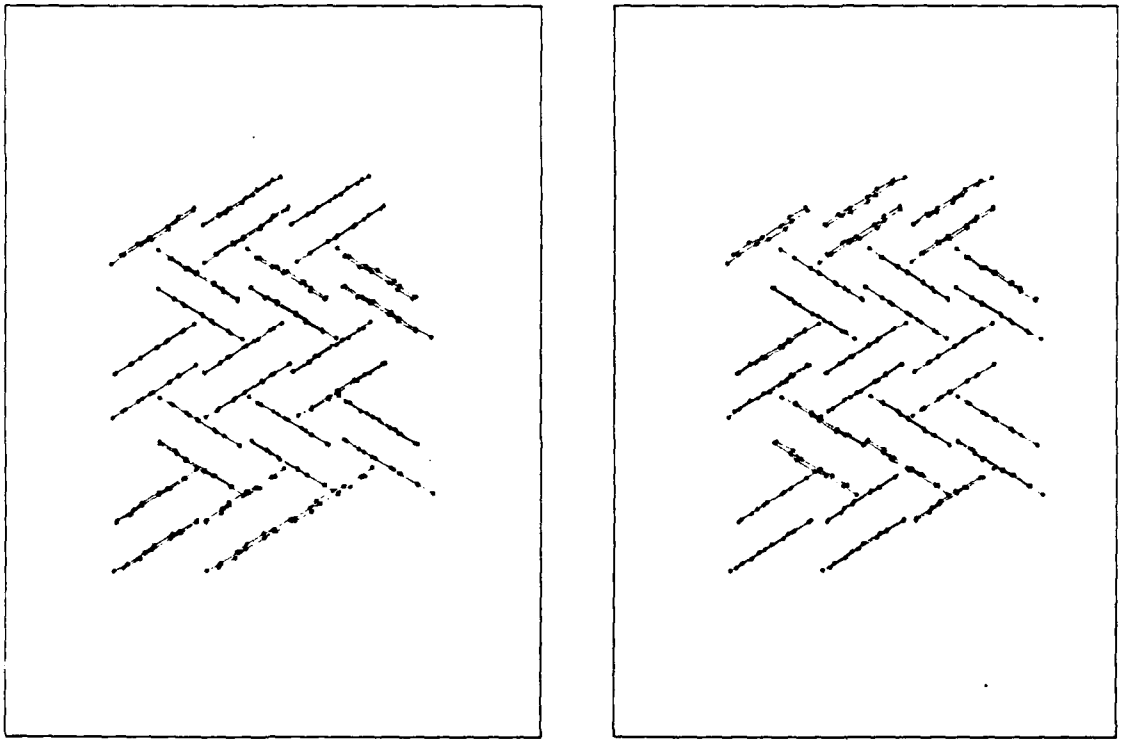


FIGURE 1. Bond Lengths and Bond Angles for Tetrazolo[1,5-f]-furazano[4,5-b]pyridine-1-oxide (**16**).

In addition to locating the position of the exocyclic oxygen, the structure determination showed, as expected, that **16** is approximately planar. The pyridofuroxan portion (C(1) through C(5), N(1) through N(3), O(1) and O(2)) is planar within the expected standard deviations. The plane of the tetrazole ring (C(5) and N(3) through N(6)) deviates from the plane of the pyridofuroxan moiety by an angle of 1 deg. With two exceptions, the bond lengths of the furoxan portion of the molecule are within three

estimated standard deviations (esd) or less of the mean bond lengths for furoxans (Reference 18). The C(1)-N(1) bond observed for **16** is 1.291(3) Å compared with the reported mean value of 1.304(8) Å; the N(2)-O(2) bond length is 1.222(2) Å compared with the mean reported value of 1.234(8) Å. However, the reported standard deviations for the mean values suggest that the observed bond lengths for the furoxan portion of **16** are within the range seen for other furoxans. The pyridine ring has a distinct variation of long and short bonds, reflecting the influence of the tetrazole and furoxan functionalities. The C(1)-N(3) and C(5)-N(3) bonds are both longer (1.377(2) and 1.354(3) Å, respectively) than the reported mean of 1.337(12) Å for pyridine C-N bonds (Reference 18). The C(2)-C(3) and C(4)-C(5) bonds are both long (1.429(3) and 1.444(3) Å), whereas, the C(3)-C(4) bond is short (1.341(3) Å) compared with the aromatic C-C bond length of 1.380(15) Å found in other pyridines (Reference 18). The latter reference does not report mean bond lengths for tetrazoles. However, the bond lengths in the tetrazole portion of **16** are the same as those found in two similar compounds (namely 7-nitro-5,6-7H-imidazolo[1,2-d]tetrazole and bis-tetrazolo[1,5-a:1',5'-c]pyrazine), within estimated standard deviations (Reference 19). There is little in the packing pattern of **16** (see Figure 2) to account for



LEFT **RIGHT**

FIGURE 2. Molecular Packing Pattern for Tetrazolo[1,5-f]-furazano[4,5-b]pyridine-1-oxide (**16**).

lower-than-expected density (1.72 versus 1.82). The molecules are slip-stacked with an inter-planar distance of 3.162 Å, which is slightly less than the expected van der Waals distance of 3.4 to 3.7 Å (Reference 20). This slip-stacking may occur to minimize direct repulsive overlap between molecules. The angle between molecular planes in adjacent stacks is 116 deg.

EXPERIMENTAL SECTION

Melting points were determined in capillary tubes using a Buchi 510 melting point apparatus. More detailed thermal behavior was determined using a Dupont 1090 Thermal Analyzer. Infrared spectra were determined in KBr disks using a Perkin-Elmer Model 1330 spectrophotometer, while FTIR spectra were recorded on a Nicolet 60SX instrument. ^{1}H-NMR spectra were determined in d_6-acetone solutions (unless stated otherwise) using an IBM NR-80 instrument; ^{13}C-NMR spectra were recorded on the same instrument operating at 20 MHz or on a Nicolet NT-200 instrument operating at 50 MHz. Mass spectra were determined using a Perkin-Elmer 5985 gas chromatography/mass spectrometer (GC/MS). **WARNING: Many of the compounds described in this report are explosives which may be subject to accidental initiation by such stimuli as friction, heat, and impact. Therefore, appropriate precautions should be taken in their handling and/or use.**

TETRAZOLO[1,5-a]PYRIDINE (**6a**)

2-Chloropyridine (**4a**) (3.00 g; 26.4 mmol) and sodium azide (2.00 g; 30.7 mmol) were heated in DMF (50 mL) at 130 to 140°C for 48 h. The solvent was removed by evaporation under reduced pressure, and the residue was recrystallized from ethanol (with decolorization) to give tetrazolo[1,5-a]pyridine (**6a**) as buff-colored crystals (0.61 g; 21%), mp 154-156°C. (This purification process appears to be both wasteful and inefficient.) IR: 1630, 1490, 1100, 770, and 755 cm^{-1}; ^{1}H-NMR: δ 7.47 (H_6), 7.85 (H_5), 8.10 (H_4), 9.12 (H_7) ($J_{4,5}$ = 8.95 Hz, $J_{4,6}$ = 1.30 Hz, $J_{4,7}$ = 0.88 Hz, $J_{5,6}$ = 6.52 Hz, $J_{5,7}$ = 3.08 Hz, $J_{6,7}$ = 6.78 Hz); ^{13}C-NMR: δ 116.19 (C_4), 117.73 (C_6), 126.89 (C_7), 133.30 (C_5), 149.52 (C_9); m/z 120 (parent ion), 92 (base peak).

4-NITROTETRAZOLO[1,5-a]PYRIDINE (**6b**)

2-Chloro-3-nitropyridine (**4b**) (0.50 g, 3.2 mmol) and sodium azide (0.50 g, 7.7 mmol) were dissolved in 10% aqueous ethanol at ambient temperature; 10% hydrochloric acid was added. The solution was then heated under reflux for 48 h. Evaporation to dryness, addition of water (ca. 10 mL), and filtration gave a buff-colored solid residue (0.45 g, 86%). Recrystallization from ethanol gave **6b** as tan needles (0.27 g), mp 171 to 173°C (dec). IR: 1635, 1545, 1520, 1490, 1345, 1320, 820, 795, 760 cm^{-1}; ^{1}H-NMR: δ 7.74(H_6), 8.88(H_5), 9.58(H_7) ($J_{5,6}$ = 7.62 Hz, $J_{5,7}$ = 0.91 Hz, $J_{6,7}$ = 6.89 Hz); ^{13}C-NMR: δ 116.75 (C_6), 132.12 (C_5), 133.16

(C_7), 137.62 (C_4), 144.65 (C_9); m/z: 165 (parent ion), 137, 107, 91, 77, 64 (base peak).

6-NITROTETRAZOLO[1,5-a]PYRIDINE (**6c**)

2-Chloro-5-nitropyridine (**4c**) (0.50 g, 3.2 mmol) was dissolved in 10% aqueous ethanol (50 mL), and sodium azide (0.50 g, 7.7 mmol) in aqueous ethanol (20 mL) was added at ambient temperature. The mixture was then warmed to redissolve the reagents, 10% hydrochloric acid (5 mL) was added, and the solution was heated under reflux for 48 h. The ethanol was removed by evaporation under reduced pressure, and the solid was filtered off to give 0.33 g, 63%. Recrystallization from ethanol gave **6c** as colorless plates, mp 139 to 41°C. IR: 1630, 1560, 1525, 1500, 1350, 1330, 1050, 800 & 730 cm^{-1}; ^{1}H-NMR: δ 8.33 (H_4), 8.58 (H_5), 10.31 (H_7) ($J_{4,5}$ = 9.82 Hz, $J_{4,7}$ = 0.94 Hz, $J_{5,7}$ = 1.94 Hz), (also contains 10% 2-azido-5-nitropyridine (**5c**), δ 7.13 (H_3), 8.57 (H_4), 9.20 (H_6) ($J_{3,4}$ = 8.90 Hz, $J_{3,6}$ = 0.65 Hz, $J_{4,6}$ = 2.93 Hz); ^{13}C-NMR: δ 116.50 (C_4), 127.29 (C_7), 127.81 (C_5), 141.28 (C_6), 150.35 (C_9), (also contains **5c**, δ 114.96 (C_3), 135.35 (C_4), 143.15 (C_5), 146.13 (C_6), 160.47 (C_2)); m/z: 165 (parent ion and base peak).

4,6-DINITROTETRAZOLO[1,5-a]PYRIDINE (**6d**)

Reaction A. 2-Chloro-3,5-dinitropyridine (**4d**) (0.10 g, 0.5 mmol) and sodium azide (0.10 g, 1.5 mmol) were dissolved in 10% aqueous ethanol (25 mL) and stirred at ambient temperature overnight. Evaporation to dryness under reduced pressure gave an orange solid mass (0.16 g), shown by ^{1}H-NMR to contain the Meisenheimer complex (**7**). ^{1}H-NMR: δ 1.10 (t, 3 H, CH_3), 3.87 (tq, 2 H, -OCH_2-, shows evidence of restricted rotation), 7.14, 8.83 (AB quartet, J = 0.80 Hz, 2 H, aromatic); IR: 2110, 1590, 1550, 1280, 1230, 1220, 1060 cm^{-1}. The orange solid (0.08 g) was redissolved in 10% aqueous ethanol (25 mL), and 10% hydrochloric acid (3 mL) was added. The solution was stirred at ambient temperature overnight. Evaporation of the ethanol and filtration gave the tetrazolopyridine (**6d**) (0.05 g, 90%) as yellow needles.

Reaction B. 2-Chloro-3,5-dinitropyridine (**4d**) (0.50 g, 2.5 mmol) and sodium azide (0.50 g, 7.7 mmol) were dissolved in 10% aqueous ethanol (50 mL). After the addition of 10% hydrochloric acid (3 mL), the solution was stirred at ambient temperature overnight. Evaporation of the ethanol under reduced pressure gave **6d** as a pale yellow solid (0.45 g, 87%) mp 123°C (dec). The best purification procedure was redissolution in 10% aqueous ethanol, followed by evaporation of the ethanol under reduced pressure and filtration. IR: 1640, 1570, 1550, 1535, 1470, 1460, 1445, 1420, 1370, 1060, 975, 740 cm^{-1}; ^{1}H-NMR: δ 9.42 (H_5), 10.81 (H_7) ($J_{5,7}$ = 1.84 Hz) (also contains 40% 2-azido-3,5-dinitropyridine (**5d**), δ 9.17 (H_4), 9.44 (H_6) ($J_{4,6}$ = 2.48 Hz)); ^{13}C-NMR: δ 126.52 (C_5), 132.91 (C_7), 136.06 (C_4), 139.57 (C_6), 148.88 (C_9) (also contains **5d**, δ 131.79 (C_4), ca. 133 (C_3), 141.74

(C_5), 145.32 (C_6), 153.77 (C_2)); m/z: 210 (parent ion), 182, 152, 106, 78 (base peak).

FURAZANO[4,5-b]PYRIDINE-1-OXIDE (**9b**)

4-Nitrotetrazolo[1,5-a]-pyridine (**6b**) (0.50 g; 3.0 mmol) was dissolved in toluene (50 mL) and heated under reflux for 4 h or until the evolution of nitrogen was complete. The solution was decolorized with charcoal and filtered, then evaporated to dryness to leave **9b** as a pale yellow solid (0.40 g, 96%). Recrystallization from cyclohexane gave pale yellow needles (0.27 g), mp 52 to 53°C. IR: 1610, 1525, 1395, 1370, 1125, 1030, 800 cm^{-1}; ^{1}H-NMR: δ 7.45 (H_6), 8.05 (H_7), 8.86 (H_5) ($J_{5,6}$ = 3.76 Hz, $J_{5,7}$ = 1.65 Hz, $J_{6,7}$ = 9.08 Hz); ^{13}C-NMR: δ 109.42 (C_8), 123.23 (C_7), 125.89 (C_6), 160.43 (C_9), 161.60 (C_5); m/z: 137 (parent ion), 107, 77, 76, 52 (base peak), 50.

6-NITROFURAZANO[4,5-b]PYRIDINE-1-OXIDE (**9d**)

Reaction A. 4,6-Dinitrotetrazolo[1,5-a]pyridine (**6d**) (0.10 g, 0.5 mmol) was placed in a test tube, and carefully heated in an oil bath to ca. 120 to 130°C. The pale yellow tetrazole melted suddenly with the evolution of gas and yellow vapor. The residue was cooled and solidified, and the sublimed to give **9d** as a yellow solid, mp 93 to 96°C.

Reaction B. 4,6-Dinitrotetrazolo[1,5-a]pyridine (**6d**) (0.35 g, 1.7 mmol) was dissolved in toluene (25 mL) and heated slowly with stirring in an oil bath. At ca. 75°C an evolution of gas commenced. The solution was heated to 95°C until the gas evolution ceased; the solution was cooled, filtered, and then evaporated to dryness to give **9d** as a yellow solid (0.28 g, 92%). Recrystallization from benzene gave yellow crystals, mp 93 to 94°C. IR: 1610, 1595, 1545, 1345, 1180, 825, 765 cm^{-1}; ^{1}H-NMR: δ 9.14 (H_7), 9.51 (H_5) ($J_{5,7}$ = 2.41 Hz); ^{13}C-NMR: δ 108.79 (C_8), 123.42 (C_7), 143.59 (C_6), 155.42 (C_5), 159.46 (C_9); m/z: 182 (parent ion), 152, 106, 78 (base peak), 76, 75.

2,3-DINITROPYRIDINE (**12**)

Furazano[4,5-b]pyridine-1-oxide (**9b**) (0.13 g, 0.95 mmol) was dissolved in 30% oleum (6 mL) and cooled in an ice bath. Hydrogen peroxide (90%, 1.5 mL) was added dropwise with stirring. The solution was allowed to warm to ambient temperature, and the reaction was allowed to continue for 24 h. Quenching on ice and extraction with dichloromethane (3 x 50 mL) gave an oil (0.13 g), whose NMR spectra indicated ca. 70% reaction. Flash chromatography (benzene/silica) gave two fractions; the first yielded a pale oil (0.08 g, 60%), triturated with hexane to give **12** as a tan solid. IR: 1600, 1560, 1540, 1370, 1355, 1080, 875 cm^{-1}; ^{1}H-NMR: δ 8.15 (dd, 1 H), 8.79-8.97 (m, 2 H); m/z: 169 (parent ion), 123, 77, 76, 53 (base

peak). The second fraction contained unreacted starting material (0.04 g). All attempts at oxidation of **9b** under milder conditions were unsuccessful. Attempted oxidation of **9d** under these conditions gave only general decomposition with copious evolution of gas.

TETRAZOLO[1,5-f]FURAZANO[4,5-b]PYRIDINE-1-OXIDE (16)

Reaction A. 3-Nitro-2,6-dichloropyridine (**13**) (1.00, 5.2 mmol) was dissolved in acetonitrile (50 mL), and sodium azide (1.00 g, 27.8 mmol) was added. The mixture was heated under reflux with stirring for 4 h, at which time the gas evolution appeared to be complete. Filtration and evaporation gave a brown/yellow solid (0.81 g, 88%) identified as **16**.

Reaction B. 3-Nitro-2,6-dichloropyridine (**13**) (1.0 g, 5.2 mmol) was dissolved in acetonitrile (50 mL), and sodium azide (1.00 g, 27.8 mmol) was added. The mixture was stirred at ambient temperature for 24 h, then filtered and evaporated to dryness to leave a yellow/tan solid (0.97 g). This solid was dissolved in benzene (50 mL), filtered, and evaporated to give a pale yellow solid (0.93 g, 95%) identified as 7-azido-6-nitrotetrazolo[1,5-a]pyridine (**15**) containing 10% of (**16**), which was not further purified. IR: 2080, 2075, 2060, 1585, 1570, 1510, 1320, 1280 cm^{-1}; ^{1}H-NMR: δ 6.86 (H_5), 7.96 (**16**), 8.48 (H_4) ($J_{4,5}$ = 8.65 Hz); m/z: 206 (parent ion). The solid **15** (0.93 g) was redissolved in benzene (50 mL) and heated under reflux for 4 h. Filtration and evaporation to dryness left **16** as an off-white solid (0.78 g, 85% overall). Best purification is by recrystallization from benzene to give off-white crystals, mp 135.5 to 137°C; sublimation gave a somewhat inferior product. IR: 1630, 1550, 1510, 1405, 800 cm^{-1}; ^{1}H-NMR: δ 7.96 (s); ^{13}C-NMR: δ 109.09 (C_9), 117.56 (C_7), 120.61 (C_8), 146.86 (C_{10}), 152.01 (C_{12}); m/z: 178 (parent ion), 150, 120, 63 (base peak).

Reaction C. 3-Nitro-2,6-dichloropyridine (**13**) (0.050 g, 2.6 mmol) was dissolved in acetonitrile (25 mL), and sodium azide (0.18 g, 2.9 mmol) was added. The reaction mixture was stirred at ambient temperature for 3 days, filtered, and evaporated to leave a tan solid (0.45 g). This solid was shown by NMR to consist of three compounds; two of the compounds were **15** and **16**. Dissolution in toluene (25 mL) and heating under reflux converted **15** to **16**; flash chromatography (chloroform/silica) gave only unreacted **13** (0.20 g, 40%) and **16** (0.21 g, 46%). No trace of monochloro intermediate was detected.

5-TRIPHENYLPHOSPHINIMINOFURAZANO[4,5]PYRIDINE-1-OXIDE (18)

Tetrazolo[1,5-f]furazano[4,5-b]pyridine-1-oxide (**16**) (0.40 g, 2.3 mmol) and triphenylphosphine (0.60 g, 2.3 mmol) were added to ethanol (50 mL) and heated under reflux for 2 h until the gas evolution was complete. The mixture was cooled and allowed to stand overnight, then filtered, and washed with ethanol to give **18** as a yellow solid (0.83 g, 90%), mp 228 to 230°C (dec.). IR: 1600, 1565, 1490, 1410, 1320,

1095, 910, 685, 520 cm^{-1}; ^{1}H-NMR: δ 6.96 (d, J = 9.38 Hz, ^{1}H), 7.20 to 8.00 (m, 16 H); m/z: 412 (parent ion), 382, 262, 183 (base peak), 108.

7-TRIPHENYLPHOSPHINIMINAZO-4-NITROTETRAZOLO[1,5-a]PYRIDINE (**19**)

7-Azido-4-nitrotetrazolo[1,5-a]pyridine (**15**) (0.44 g, 2.1 mmol) and triphenylphosphine (0.54 g, 2.1 mmol) were stirred in ethanol (25 mL) at ambient temperature for 2 h. The resultant orange solid was filtered and washed with ethanol to give **19** (0.86 g, 88%), mp 98 to 100°C (dec). IR: 1605, 1500, 1420, 1330, 1205, 1180, 1110, 1095, 910, 720, 690, 520 cm^{-1}; ^{1}H-NMR: δ 6.80 to 8.50 (br m); m/z: 440 (no parent ion), 412, 382, 304, 262, 183 (base peak).

7-TRIPHENYLPHOSPHINIMINO-4-NITROTETRAZOLO[1,5-a]PYRIDINE (**20**)

Reaction A. 7-Azido-4-nitrotetrazolo[1,5-a]pyridine (**15**) (0.38 g, 1.8 mmol) and triphenylphosphine (0.45 g, 1.7 mmol) were dissolved in benzene (25 mL) and stirred at ambient temperature for 2 h. The resultant yellow precipitate was filtered, washed with benzene, and dried to give **20** (0.56 g, 74%), mp 180°C (dec). IR: 1600, 1570, 1500, 1420, 1190, 1135, 1100, 930, 915, 710, 690, 520 cm^{-1}; ^{1}H-NMR: δ 6.85 to 8.35 (br m); m/z: 440 (parent ion), 412, 382, 366, 304, 277, 262, 183 (base peak), 152, 108.

Reaction B. The orange powder (**19**) (0.40 g, 0.9 mmol) was suspended in ethanol (25 mL) and was heated under reflux with the evolution of gas. When the gas evolution ceased (ca. 2 h) the mixture was cooled, and the yellow solid was filtered, washed with ethanol, and dried to give **20** (0.34 g, 90%). The yellow solid (**20**) (0.20 g, 0.5 mmol) was suspended in toluene (25 mL) and was heated under reflux with the evolution of gas. When the gas evolution ceased and the solid dissolved, the solution was cooled and evaporated to half volume, whereupon a yellow crystalline solid precipitated. Filtration and recrystallization from toluene gave **18** (0.14 g, 75%), identified by IR and ^{1}H-NMR

5-AMINOFURAZANO[4,5-b]PYRIDINE-1-OXIDE (**21**)

5-Triphenylphosphiniminofurazano[4,5-b]pyridine-1-oxide (**18**) (1.2 g, 2.9 mmol) was suspended in glacial acetic acid (10 mL), and concentrated hydrochloric acid (5 mL) was added at ambient temperature. The solid immediately went into solution, which was stirred overnight at ambient temperature to give a white precipitate identified as the amine hydrochloride salt. Filtration and stirring the solid in water containing an excess of potassium carbonate gave a yellow solid (0.28 g, 63%) identified as **21**. The acetic acid mother liquors were quenched with water (250 mL), filtered to remove the triphenylphosphine and basified with potassium carbonate. Continuous extraction with dichloromethane for 3 days yielded a further 0.16 g solid (total yield 0.44 g, 98%). Recrystallization gave **21** as yellow crystals, mp 234 to 236°C (dec). IR: 3360, 3110, 1670, 1620, 1600, 1510, 1480, 1235, 1120,

1015 cm^{-1}; ^{1}H-NMR: δ 6.91 (H_6), 7.61 (H_7) ($J_{6,7}$ = 9.46 Hz); ^{13}C-NMR (d_6-DMSO): δ 106.23 (C_8), 121.58 (C_6), 121.84 (C_7), 160.03 (C_9), 161.97 (C_5); m/z: 152 (parent ion), 79 (base peak), 52.

5-ACETAMINOFURAZANO[4,5-b]PYRIDINE-1-OXIDE (22)

5-Aminofurazano[4,5-b]pyridine-1-oxide (**21**) (0.10 g, 0.7 mmol) was added to glacial acetic acid (3 mL) and acetic anhydride (3 mL) and heated under reflux overnight. The solution was cooled and quenched in water (30 mL) and neutralized with potassium carbonate. Extraction with dichloromethane (3 x 25 mL) gave a pale yellow solid (0.125 g, 98%). Recrystallization from ethanol gave **22** as a pale yellow powder, mp 187 to 190°C. IR: 3250, 1710, 1600, 1580, 1500, 1430, 1400, 1325, 1255, 1200, 1110, 1030, 1005, 995, 835 cm^{-1}; ^{1}H-NMR: δ 2.31 (s, 3 H, $COCH_3$), 7.99 (H_6), 8.34 (H_7) ($J_{6,7}$ = 9.70 Hz); ^{13}C-NMR (d_6-DMSO): δ 24.44 (CH_3), 107.15 (C_8), 120.57 (C_6), 124.43 (C_7), 158.01 (C_9), 170.78 (CO & C_5); m/z: 194 (parent ion), 152, 95, 79, 64, 52, 43 (base peak).

SINGLE CRYSTAL X-RAY STRUCTURE OF TETRAZOLO[1,5-f]FURAZANO[4,5-b]-PYRIDINE-1-OXIDE (16)

Tetrazolo[1,5-f]furazano[4,5-b]-pyridine-1-oxide (**16**) crystallized as salmon-colored platelets from benzene in space group $P2_12_12_1$, Z = 4, D_x = 1.719. A crystal of dimensions 0.06 x 0.32 x 0.56 mm with {001} platelet faces was used for data collection on a Nicolet R3. Unit cell parameters a = 5.961(1), b = 9.968(2), c = 11.589(2) Å were determined from a least-squares fit of 25 computer-centered reflections with 2θ values ranging from 8 to 28 deg (Mo K_α). At variable scan speeds of 2-6°/min over a 2θ range 4-54° for octants $\bar{h}k\bar{T}$, $\bar{h}kl$, $hk\bar{T}$, hkl with monochromated Mo K_α radiation. at room temperature (291 K), 2 θ/θ intensity data were collected. Three check reflections ((210), (01-2), and (-141)), collected every 93 reflections, were constant. All data reduction and structure solution/refinement calculations were performed with SHELXTL (Reference 21). The 3311 observations were corrected for Lorentz and polarization effects. Because of the crystal shape, numerical Gaussian absorption corrections (μm = 1.31 cm^{-1}) were applied; minimum and maximum transmission factors were 0.957 and 0.991, respectively. Equivalent reflections were merged (R_{merge} = 0.0106) to yield 1511 unique data of which 1370 with $|F_o| > 4\sigma(F)$ were used in refinement. With the inclusion of four additional reflections in the starting set, the positions of all C, N, and O atoms were observed on the first E_{map} obtained by direct, multisolution methods. All N and O atoms and C(1), C(5) were refined anisotropically; C(2), C(3), C(4) were refined isotropically. The two H atoms were refined as "riding" on their adjacent carbon atoms but with unconstrained isotropic thermal parameters. The 105 parameters were refined with the blocked cascade algorithm of SHELXTL (Reference 21) and with weights $w = 1/[\sigma^2(F) + 0.0009F^2]$. Maximum shift/esd ratios were less than 0.05 for the final refinement cycles. Final agreement factors were R = 0.040, R_w = 0.054, goodness of fit = 1.39 ($R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma(|F_o|)^2]^{1/2}$).

Final difference Fourier maps had peaks and troughs ranging from +0.40 to 0.28 $e^-/Å^3$. Final atomic coordinates are given in Table 4. Tables 5 through 8 give the bond lengths, the bond angles, the anisotropic thermal parameters, and the hydrogen coordinates and isotropic thermal parameters.

TABLE 4. Atom Coordinates (x 10^4) and Temperature Factors (Å x 10^3) for Tetrazolo[1,5-f]furazano[4,5-b]pyridine-1-oxide (16).

Atom	x	y	z	U_{eq}/U_{iso}
C(1)	2844(3)	8444(2)	1751(2)	37(1)[a]
C(2)	3708(3)	8126(2)	2854(2)	37(1)
C(3)	2653(4)	8492(2)	3915(2)	44(1)
C(4)	747(4)	9203(2)	3843(2)	47(1)
C(5)	152(4)	4553(2)	2274(2)	43(1)[a]
N(1)	4032(3)	8008(2)	898(2)	53(1)[a]
N(2)	5549(3)	7428(2)	2656(2)	44(1)[a]
N(3)	874(3)	9166(2)	1738(2)	40(1)[a]
N(4)	289(3)	4644(2)	4179(2)	49(1)[a]
N(5)	-1969(4)	10279(2)	1261(2)	58(1)[a]
N(6)	-1960(3)	10241(2)	2437(2)	56(1)[a]
O(1)	5810(3)	7346(2)	1421(2)	54(1)[a]
O(2)	6987(3)	6892(2)	3251(2)	61(1)[a]

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 5. Bond Lengths for Tetrazolo[1,5-f]furazano-[4,5-b]pyridine-1-oxide (16).

Bond	Length, Å	Bond	Length, Å
C(1)-C(2)	1.414(3)	C(1)-N(1)	1.291(3)
C(1)-N(3)	1.377(2)	C(2)-C(3)	1.429(3)
C(2)-N(2)	1.320(3)	C(3)-C(4)	1.341(3)
C(4)-C(5a)	1.444(3)	C(5)-C(4a)	1.444(3)
C(5)-N(3a)	1.354(3)	C(5)-N(6a)	1.321(3)
N(1)-O(1)	1.389(3)	N(2)-O(1)	1.441(3)
N(2)-O(2)	1.222(2)	N(3)-C(5a)	1.354(3)
N(3)-N(4a)	1.356(3)	N(4)-N(3a)	1.356(3)
N(4)-N(5a)	1.290(3)	N(5)-N(6)	1.362(3)
N(5)-N(4a)	1.290(3)	N(6)-C(5a)	1.321(3)

TABLE 6. Bond Angles for Tetrazolo[1,5-f]furazano-[4,5-b]pyridine-1-oxide (16).

Bond	Angle, deg	Bond	Angle, deg
C(2)-C(1)-N(1)	114.7(2)	C(2)-C(1)-N(3)	115.9(2)
N(1)-C(1)-N(3)	129.4(2)	C(1)-C(2)-C(3)	124.1(2)
C(1)-C(2)-N(2)	105.3(2)	C(3)-C(2)-N(2)	130.6(2)
C(2)-C(3)-C(4)	117.0(2)	C(3)-C(4)-C(5a)	119.8(2)
C(4a)-C(5)-N(3a)	121.5(2)	C(4a)-C(5)-N(6a)	131.0(2)
N(3a)-C(5)-N(6a)	107.6(2)	C(1)-N(1)-O(1)	104.1(2)
C(2)-N(2)-O(1)	107.0(2)	C(2)-N(2)-O(2)	135.6(2)
O(1)-N(2)-O(2)	117.4(2)	C(1)-N(3)-C(5a)	121.7(2)
C(1)-N(3)-N(4a)	128.9(2)	C(5a)-N(3)-N(4a)	109.4(2)
N(3a)-N(4)-N(5a)	105.0(2)	N(6)-N(5)-N(4a)	112.3(2)
N(5)-N(6)-C(5a)	105.8(2)	N(1)-O(1)-N(2)	108.9(1)

TABLE 7. Anisotropic Thermal Parameters ($Å^2 \times 10^3$) for Tetrazolo[1,5-f]furazano[4,5-b]pyridine-1-oxide (16).[a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	40(1)	34(1)	38(1)	-0(1)	-1(1)	-2(1)
C(5)	42(1)	34(1)	53(1)	3(1)	4(1)	1(1)
N(1)	55(1)	57(1)	45(1)	-0(1)	4(1)	9(1)
N(2)	41(1)	41(1)	50(1)	-0(1)	-2(1)	2(1)
N(3)	40(1)	35(1)	44(1)	3(1)	-4(1)	-2(1)
N(4)	52(1)	42(1)	54(1)	-8(1)	-14(1)	0(1)
N(5)	51(1)	47(1)	77(1)	9(1)	-14(1)	5(1)
N(6)	46(1)	44(1)	76(1)	2(1)	-1(1)	8(1)
O(1)	47(1)	58(1)	55(1)	-4(1)	8(1)	13(1)
O(2)	48(1)	60(1)	76(1)	4(1)	-15(1)	13(1)

[a] The anisotropic temperature factor exponent takes the form: $-2\Pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \ldots + 2hka^*b^*U_{12})$.

TABLE 8. Hydrogen coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å \times 10^3$) for Tetrazolo[1,5-f]-furazano[4,5-b]pyridine-1-oxide (16).

Atom	x	y	z	U
H(3)	3282	8243	4647	50(6)
H(4)	-19	9475	4533	99(10)

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